Docket No. 242837US0X

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Dominic PRATT, et al.

GAU:

SERIAL NO: 10/661,609

EXAMINER:

FILED: September 15, 2003

FOR: HAIR DYE COMPOSITION AND DYEING METHOD

REQUEST FOR PRIORITY

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

☐ Full benefit of the filing date of U.S. Application Serial Number , filed , is claimed pursuant to the provisions of **35 U.S.C. §120.**

☐ Full benefit of the filing date(s) of U.S. Provisional Application(s) is claimed pursuant to the provisions of **35 U.S.C. §119(e):** **Application No.** **Date Filed**

■ Applicants claim any right to priority from any earlier filed applications to which they may be entitled pursuant to the provisions of **35 U.S.C. §119**, as noted below.

In the matter of the above-identified application for patent, notice is hereby given that the applicants claim as priority:

COUNTRY	APPLICATION NUMBER	MONTH/DAY/YEAR
European	02020528.2	September 16, 2002

Certified copies of the corresponding Convention Application(s)

■ are submitted herewith

☐ will be submitted prior to payment of the Final Fee

☐ were filed in prior application Serial No. filed

☐ were submitted to the International Bureau in PCT Application Number
Receipt of the certified copies by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

☐ (A) Application Serial No.(s) were filed in prior application Serial No. filed ; and

☐ (B) Application Serial No.(s)

- ☐ are submitted herewith
- ☐ will be submitted prior to payment of the Final Fee

Respectfully Submitted,

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10/661,609

Europäisches Patentamt	European Patent Office	Office européen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.	The attached documents are exact copies of the European patent application described on the following page, as originally filed.	Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr.	Patent application No.	Demande de brevet n°
	02020528.2	

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 02020528.2
Demande no:

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Hair dye composition and dyeing method

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

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A61K7/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

HAIR DYE COMPOSITION AND DYEING METHOD

Technical Field

The present invention relates to a hair dye composition that provides a high dyeing power, can strongly impart the hair with extremely vivid colour, has less colour fade over time and can deliver a wide range of colours.

Background Art

Hair dyes can be classified by the dye to be used or by whether they have any bleaching action on melanin. Typical examples include a two-part permanent hair dye composed of a first part containing an alkaline agent, an oxidation dye and optionally a direct dye such as a nitro dye and a second part containing an oxidizing agent; and a one-part semi-permanent hair dye containing an organic acid or an alkaline agent, and at least one direct dye such as an acid dye, a basic dye or a nitro dye.

The above-described permanent hair dye is however accompanied with the drawbacks that the colour tone imparted by an oxidation dye is not so vivid and that the colour of the hair dyed with a vivid-colour producing nitro dye ordinarily employed as a direct dye markedly fades over time and becomes dull quickly even if the colour tone immediately after dyeing is very vivid (Japanese Patent Application Laid-Open (*Kokai*) No. Hei 6-271435).

It is common practice to combine direct dyes and oxidative dyes in permanent products to provide more vivid colour, however currently available direct dyes do not usually perform satisfactorily. The number of direct dyestuff that can be used in combination with oxidative dyes is limited by the necessity that they must be stable to alkaline peroxide during the dyeing process.

A variety of cationic direct dyes and nitro dyes have been used in permanent hair dye products to add brilliance and vividness to shades. However, in both cases the colour fades very quickly due to the loss of the direct dye from washing and light, especially on damaged or porous hair.

Disclosure of the Invention

An object of the present invention is to provide a hair dye composition comprising as a direct dye a dissociative phenyl azo dye or naphthyl azo dye which can strongly impart the hair with a vivid colour without decomposition of the dye upon hair dyeing, has excellent resistance to light, washing, perspiration, friction and heat. The dye is stable in alkaline conditions and stable against an oxidizing agent, has high hair dyeing power and shows less colour fade over time.

Another object is to provide a hair dyeing method by applying the above mentioned azo dye to the hair.

The present inventors have found that dissociative phenyl azo dyes or naphthyl azo dyes of the general structure (I) below and the resulting dyeing composition can strongly impart the hair with a vivid colour selected from a wide range of different colours without decomposition of the dye upon hair dyeing, and exhibits excellent resistance to fading from light, washing, perspiration, friction and heat.

In one aspect of the present invention, there is thus provided a hair dyeing composition comprising a dissociative azo dye represented by the following general formula (1):

General formula (I)

$$A\text{-}N{=}N\text{-}B$$

where "A" represents a phenyl or naphthyl group wherein these groups may be substituted wherein the phenyl or naphthyl groups do not contain sulfo or carboxyl groups or

quaternary ammonium groups; and "B" represents an atomic group required for the compound represented by the general formula (1) to form a dissociative azo dye, which is free from sulfo or carboxyl groups and quaternary ammonium groups.

The number of carbon atoms in the phenyl or naphthyl group represented by "A" including optional substituents on the phenyl or naphthyl group is preferably 6 to 20, more preferably 6 to 10 .

The phenyl or naphthyl group represented by the "A" is preferably derived from a diazo component that per se is known in the art.

Herein, the diazo component means a partial structure introduced by converting an aromatic compound with a substituent amino group to a diazo compound and allowing the resulting diazo compound to be subjected along with a coupler to diazo-coupling reaction, which belongs to a concept commonly used in the field of azo dye.

In other words, the diazo component means a substituent prepared by eliminating an amino group from an amino-substituted aromatic compound possibly subjected to diazo reaction, to render the resulting product that is a monovalent group.

In the general formula (1), the phenyl or naphthyl group represented by the "A" may contain a substituent and in that case, the substituent includes for example halogen atom, cyclic, straight-chain or branched-chain alkyl group (including cycloalkyl group), cyclic, straight-chain or branched-chain alkenyl group (including cycloalkenyl group), alkynyl group, aryl group, hetero-ring group, cyano group, hydroxy group, nitro group, alkoxy group, aryloxy group, silyloxy group, hetero-ring oxy group, acyloxy group, carbamoyloxy group, alkoxycarbonyloxy group, aryloxycarbonyloxy, amino group (including anilino group), acylamino group, aminocarbonylamino group, alkoxycarbonylamino group, aryloxycarbonylamino group,

sulfamoylamino group, alkylsulfonylamino group, arylsulfonylamino group, mercapto group, alkylthio group, arylthio group, hetero-ring thio group, sulfamoyl group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, acyl group; alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, arylazo group, hetero-ring azo group, imide group, phosphino group, phosphinyl group, phosphinyloxy group, phosphinylamino group, and silyl group. More specifically, the substituent includes for example halogen atom (for example, chlorine atom, bromine atom, iodine atom), alkyl group (linear or branched or cyclic alkyl group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, methyl, ethyl, n-propyl, isopropyl, t-butyl, n-octyl, 2-chloroethyl, 2-cyanoethyl, 2-ethylhexyl, cyclopropyl, cyclopentyl), alkenyl group (linear or branched or cyclic alkenyl group with 2 to 10 carbon atoms, preferably 2 to 6 carbon atoms, for example, vinyl, allyl, prenyl, cyclopenten-1-yl), alkynyl group (alkynyl group with 2 to 10 carbon atoms, preferably 2 to 6 carbon atoms, for example, ethynyl, propargyl), aryl group (aryl group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, for example, phenyl, p-tolyl, naphthyl, 3-chlorophenyl, 2-aminophenyl), hetero-ring group (monovalent group with one to 12 carbon atoms, preferably 2 to 6 carbon atoms, which is recovered by eliminating one hydrogen atom from an aromatic or non-aromatic hetero-ring compound, 5-membered or 6-membered; for example, 1-pyrazolyl, 1-imidazolyl, 2-furyl, 2-thienyl, 4-pyrimidinyl, 2-benzothiazolyl), cyano group, hydroxy group, nitro group, alkoxy group (linear or branched or cyclic alkoxy group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, methoxy, ethoxy, isopropoxy, t-butoxy, cyclopentyloxy, 2-buten-1-yloxy, 2-methoxyethoxy), aryloxy group (aryloxy group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, for example, phenoxy, 2-methylphenoxy, 4-

t-butylphenoxy, 3-nitrophenoxy), silyloxy group (silyloxy group with 3 to 10 carbon atoms, preferably 3 to 6 carbon atoms, for example, trimethylsilyloxy, t-butyldimethylsilyloxy), hetero-ring oxy group (hetero-ring oxy group with one to 12 carbon atoms, preferably 2 to 6 carbon atoms, for example, 1-phenyltetrazole-5-oxy, 2-tetrahydropyranyloxy), acyloxy group (acyloxy group with one to 12 carbon atoms, preferably one to 8 carbon atoms, for example,, formyloxy group, acetyloxy, pivaloyloxy, benzoyloxy, p-methoxyphenylcarbonyloxy), carbamoyloxy group (carbamoyloxy group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, N,N-dimethylcarbamoyloxy, N,N-diethylcarbamoyloxy, morpholinocarbonyloxy, N-n-octylcarbamoyloxy), alkoxycarbonyloxy group (alkoxycarbonyloxy group with 2 to 10 carbon atoms, preferably 2 to 6 carbon atoms, for example, methoxycarbonyloxy, ethoxycarbonyloxy, t-butoxycarbonyloxy, n-octyloxycarbonyloxy), aryloxycarbonyloxy group (aryloxycarbonyloxy group with 7 to 12 carbon atoms, preferably 7 to 10 carbon atoms, for example, phenoxycarbonyloxy, p-methoxyphenoxycarbonyloxy), amino group (amino group, alkylamino group with one to 10 carbon atoms, preferably one to 6 carbon atoms, anilino group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, or hetero-ring amino group with one to 12 carbon atoms, preferably 2 to 6 carbon atoms, including for example amino, methylamino, dimethylamino, anilino, N-methyl-anilino, diphenylamino, imidazol-2-ylamino, pyrazol-3-ylamino), acylamino group (alkylcarbonylamino group with one to 10 carbon atoms, preferably one to 6 carbon atoms, arylcarbonylamino group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, or hetero-ring carbonylamino group with 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms, including for example formylamino, acetylamino, pivaloylamino, benzoylamino, pyridine-4-carbonylamino, thiphene-2-carbonylamino),

aminocarbonylamino group (aminocarbonylamino with one to 12 carbon atoms, preferably one to 6 carbon atoms, for example, carbamoylamino, N,N-dimethylaminocarbonylamino, N,N-diethylaminocarbonylamino, morpholin-4-ylcarbonylamino), alkoxycarbonylamino group (alkoxycarbonylamino group with 2 to 10 carbon atoms, preferably 2 to 6 carbon atoms, for example, methoxycarbonylamino, ethoxycarbonylamino, t-butoxycarbonylamino), aryloxycarbonylamino group (aryloxycarbonylamino group with 7 to 12 carbon atoms, preferably 7 to 9 carbon atoms, for example, phenoxycarbonylamino, p-chlorophenoxycarbonylamino, 4-methoxyphenoxycarbonylamino), sulfamoylamino group (sulfamoylamino group with zero to 10 carbon atoms, preferably zero to 6 carbon atoms, for example sulfamoylamino, N,N-dimethylaminosulfonylamino, N-(2-hydroxyethyl)sulfamoylamino), alkylsulfonylamino group (alkylsulfonylamino group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, methylsulfonylamino, butylsulfonylamino), arylsulfonylamino group (arylsulfonylamino group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, for example, phenylsulfonylamino, 2,3,5-trichlorophenylsulfonylamino group, p-methylphenylsulfonylamino), mercapto group, alkylthio group (alkylthio group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example methylthio, ethylethio, butylthio), arylthio group (arylthio with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, for example, phenylthio, p-chlorophenylthio, m-methoxythio), hetero-ring thio group (hetero-ring thio group with 2 to 10 carbon atoms, preferably one to 6 carbon atoms, for example 2-benzothiazolylthio, 1-phenyltetrazol-5-ylthio), sulfamoyl group (sulfamoyl group with zero to 10 carbon atoms, preferably zero to 6 carbon atoms, for example, sulfamoyl, N-ethylsulfamoyl, N,N-dimethylsulfamoyl, N-acetylsulfamoyl, N-benzoylsulfamoyl), alkylsulfinyl group (alkylsulfinyl group

with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, methylsulfinyl, ethylsulfinyl), arylsulfinyl group (arylsulfinyl group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, for example, phenylsulfinyl, p-methylphenylsulfinyl), alkylsulfonyl group (alkylsulfonyl group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, methylsulfonyl, ethylsulfonyl), arylsulfonyl group (arylsulfonyl group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, for example, phenylsulfonyl, p-chlorophenylsulfonyl), acyl group (formyl group, alkylcarbonyl group with 2 to 10 carbon atoms, preferably 2 to 6 carbon atoms, or arylcarbonyl group with 7 to 12 carbon atoms, preferably 7 to 9 carbon atoms, including for example acetyl, pivaloyl, 2-chloroacetyl, benzoyl, 2,4-dichlorobenzoyl), alkoxycarbonyl group (alkoxycarbonyl group with 2 to 10 carbon atoms, preferably 2 to 6 carbon atoms, for example, methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl, isobutyloxycarbonyl), aryloxycarbonyl group (aryloxycarbonyl group with 7 to 12 carbon atoms, preferably 7 to 9 carbon atoms, for example, phenoxycarbonyl, 2-chlorophenoxycarbonyl, 3-nitrophenoxycarbonyl, 4-t-butylphenoxycarbonyl), carbamoyl group (carbamoyl group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N-(2-hydroxyethyl)carbamoyl, N-(methylsulfonyl)carbamoyl), arylazo group (arylazo group with 6 to 12 carbon atoms, preferably 6 to 8 carbon atoms, for example phenylazo, p-chlorophenylazo), hetero-ring azo group (hetero-ring azo group with one to 10 carbon atoms, preferably one to 6 carbon atoms, for example, pyrazol-3-ylazo, thiazol-2-ylazo, 5-ethylthio-1,3,4-thiadiazol-2-ylazo), imide group (imide group with 2 to 10 carbon atoms, preferably 4 to 8 carbon atoms, for example, N-succinimide, N-phthalimide), phosphino group (phosphino group with 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms, for example, dimethylphosphino,

diphenylphosphino, methylphenoxyphosphino), phophinyl group (phosphinyl group with 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms, for example phosphinyl, diethoxyphosphinyl), phosphinyloxy group (phosphinyloxy group with 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms, for example, diphenoxyphosphinyloxy, dibutoxyphosphinyloxy), phosphinylamino group (phosphinylamino group with 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms, for example, dimethoxyphosphinylamino, dimethylaminophosphinylamino), and silyl group (silyl group with 3 to 12 carbon atoms, preferably 3 to 8 carbon atoms, for example, trimethylsilyl, t-butyldimethylsilyl, phenyldimethylsilyl). In case that these groups are groups with a possibility of additional substitution, these groups may further contain substituents, and preferably, such substituents then include the groups with the same meaning as described as the preferable substituent for the phenyl or naphthyl group represented by A. In case that these groups are substituted with 2 or more substituents, the substituents may be the same or different.

Particularly preferably, the substituent for the phenyl or naphthyl group represented by A is halogen atom, alkyl group, aryl group, hetero-ring group, cyano group, hydroxy group, nitro group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, aminocarbonylamino group, alkoxycarbonylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, hetero-ring thio group, sulfamoyl group, alkylsulfonyl group, arylsulfonyl group, acyl group, alkoxycarbonyl group, and carbamoyl group; more preferably, the substituent is halogen atom, alkyl group, cyano group, hydroxy group, nitro group, alkoxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, carbamoyl group, sulfamoyl group, alkylsulfonyl group and arylsulfonyl group.

Above all, the substituent is preferably an electron withdrawing group having Hammet's constant value σ_p of not less than 0.1, such as halogen atom, cyano group, nitro group, sulfamoyl group, alkylsulfonyl group and arylsulfonyl group. Hammet's rule is an empirical rule suggested by L. P. Hammet in 1935 in order to quantitatively discuss the effects of a substituent of a benzen derivative on the reaction or equilibrium thereof, which rule has been widely acknowledged. According to the Hammet's rule, there are two kinds of values, σ_p and σ_m values as a coefficient of substitution. These values are described in many books, for instance, J. A. Dean "Lange's Handbook of Chemistry", 12nd edition, 1979 (McGraw-Hill); "Kagakunoryouiki-zoukan" 122, 96-103, 1979 (Nankodo); and "Chemical Review", 91, 165-195, 1991 recite the values.

Throughout the specification any reference to a hetero-ring compound means a compound comprising a heteroatom containing group containing at least one heteroatom selected from N, O and S. B in the azo dye represented by the general formula (1) represents an atomic group essential for the formation of a dissociative azo dye from the compound represented by the general formula (1) and is preferably derived from a coupler component. Herein, the coupler component means a partial structure derived from a coupler compound capable of reacting with a diazonium salt to give an azo dye. The concept is commonly used in the field of azo dye. B in the azo dye represented by the general formula (1) has preferably 3 to 30 carbon atoms, more preferably 3 to 20 carbon atoms, most preferably 3 to 12 carbon atoms, inclusive of the substituents therein.

The coupler component is preferably a coupler component known in the field of silver halide colour photographic materials, and as such, use can be made of the backbone moiety of a colour coupler (the moiety serving as a dye chromophore via coupling with an aromatic amine-based

developing agent, such as p-phenylenediamine), which is described in detail in Research Disclosure 37038 (February 1995), page 80-85, and 87-89.

The coupler known as a coupler forming yellow-colored image in the field of silver halide colour photographic materials includes for example couplers of pivaloylacetamide type, benzoylacetamide type, malondiester type, malondiamide type, dibenzoylmethane type, benzothiazolylacetamide type, malonestermonoamide type, benzooxazolylacetamide type, benzoimidazolylacetamide type, cyanoacetamide type, cycloalkylcarbonylacetamide type, indolin-2-ylacetamide type, quinazolin-4-on-2-ylacetamide type described in USP 5,021,332, and the benzo-1,2,4-thiadiazine-1,1,-dioxid-3-ylacetamide type described in USP 5,021,330, the coupler described in EP 421221A, the coupler described in USP 5,455,149, the coupler described in EPA 0622673, the couplers of 3-indoloylacetamide type described in EPA 0953871, 0953872 and 0953873, as preferable coupler backbones.

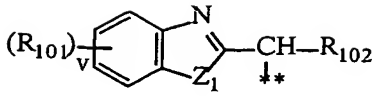
The coupler known as a coupler forming magenta-colored image in the field of silver halide colour photographic materials includes for example couplers of 5-pyrazolone type, 1H-pyrazolo[1,5-a]benzimidazole type, 1H-pyrazolo[5,1-c][1,2,4]triazole type, 1H-pyrazolo[1,5-b][1,2,4]triazole type, 1H-imidazo[1,2-b]pyrazole type, cyanoacetophenone type, the active propene type described in WO 93/01523, and the enamine type described in WO 93/07534, the 1H-imidazo[1,2-b][1,2,4]triazole type coupler and the coupler described in USP 4,871,652, as preferable coupler backbones.

The coupler known as a coupler forming cyan-colored image in the field of silver halide colour photographic materials includes for example couplers of phenol type, naphthol type, the 2,5-diphenylimidazole type 1H-pyrrolo[1,2-b][1,2,4]triazole type, and 1H-pyrrolo[2,1-c][1,2,4]triazole type as described in EPA 0249453, the pyrrole type described in Japanese Patent Laid-open Nos.

188137/1992 and 190347/1992, 3-hydroxypyridine type described in Japanese Patent Laid-open No. 315736/1989, pyrrolopyrazole type described in Japanese Patent Laid-open No. 174429/1992, the pyrroloimidazole type described in Japanese Patent Laid-open No. 174429/1992, and the pyrazolopyrimidine type described in USP 4,950,585, and the pyrrolotriazine type coupler described in Japanese Patent Laid-open No. 204730/1992, the coupler described in USP 5,104,783, the coupler described in USP, 5,162,196, and the coupler described in EP 0556700, as preferable coupler backbones.

The group represented by B in the azo dye represented by the general formula (1) preferably includes groups represented by the following structures (B-1) to (B-12).

(B-1)



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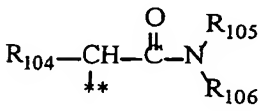

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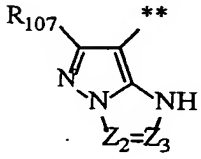

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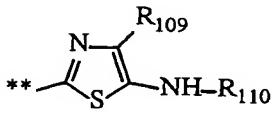

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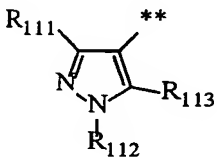

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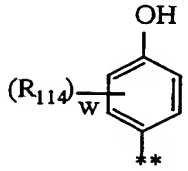
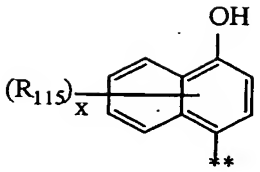
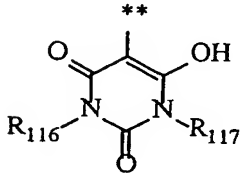


(B-7)



(B-8)



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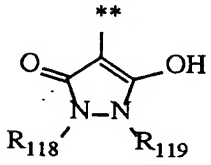
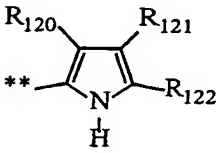
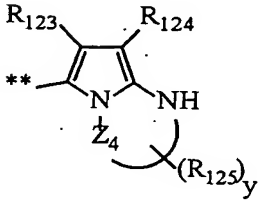


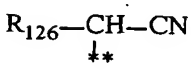
(B-10)



(B-11)



(B-12)



In the formulas, the symbol "**" expresses the position where the groups bind to the azo group in the general formula (1).

In the formula (B-1), R_{101} represents halogen atom, alkyl group, aryl group, hetero-ring group, cyano group, alkoxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, sulfamoyl group, alkylsulfonyl group, or carbamoyl group. R_{102} represents cyano group, alkylsulfonyl group, arylsulfonyl group, acyl group, alkoxycarbonyl group, aryloxycarbonyl group, or carbamoyl group. Z_1 represents oxygen atom, sulfur atom, or $-N(R_{103})-$. R_{103} represents hydrogen atom, alkyl group, aryl group or hetero-ring group. "v" represents an integer of 0 to 4. Provided that v is a plural number, the R_{101} groups in the number "v" may be the same or different. R_{101} is preferably halogen atom, acylamino group, alkylsulfonylamino group, sulfamoyl group, and carbamoyl group. R_{102} is preferably cyano group, and carbamoyl group. Z_1 is preferably oxygen atom, sulfur atom, or $-N(R_{103})-$ where R_{103} is an alkyl group.

In the formula (B-2), R_{104} represents cyano group, alkylsulfonyl group, arylsulfonyl group, acyl group, alkoxycarbonyl group, aryloxycarbonyl group, or carbamoyl group; R_{105} and R_{106} independently represent hydrogen atom, alkyl group, aryl group, or hetero-ring group. Preferably, R_{104} is cyano group, acyl group, and carbamoyl group, while one of R_{105} and R_{106} is preferably hydrogen atom.

In the formula (B-3), R_{107} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; Z_2 and Z_3 independently represent $-C(R_{108})=$, or $-N=$; R_{108} represents

alkyl group, aryl group, hetero-ring group, alkylthio group, arylthio group, alkoxycarbonyl group, or carbamoyl group. Provided that Z_2 and Z_3 both represent $-C(R_{108})=$, two R_{108} groups may be the same or different or may bind together to form a carbon ring or a hetero-ring. R_{107} is preferably hydrogen atom, alkyl group and aryl group, more preferably hydrogen atom and alkyl group, and R_{108} is preferably alkyl group, aryl group, and hetero-ring group, more preferably alkyl group.

In the formula (B-4), R_{109} represents alkyl group, aryl group or hetero-ring group, and R_{110} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, acyl group, alkylsulfonyl group or arylsulfonyl group. R_{109} is preferably alkyl group and aryl group, and R_{110} is preferably hydrogen atom and alkyl group.

In the formula (B-5), R_{111} represents hydrogen atom, alkyl group, aryl group, alkoxy group, amino group (including anilino group), alkoxycarbonyl group, cyano group, acylamino group, or carbamoyl group; R_{112} represents hydrogen atom, alkyl group, aryl group, or hetero-ring group; R_{113} represents hydroxy group or amino group. R_{111} is preferably alkoxycarbonyl group, cyano group, and carbamoyl group; R_{112} is preferably alkyl group and aryl group.

In the formula (B-6), R_{114} represents halogen atom, alkyl group, aryl group, hetero-ring group, nitro group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkoxycarbonylamino group, aminocarbonylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, hetero-ring thio group, alkoxycarbonyl group, or carbamoyl group; "w" represents an integer of 0 to 4. Provided that "w" is a plural number, the R_{114} groups in the number "w" may be the same or different. R_{114} is preferably halogen atom, alkyl group, acylamino group, alkoxycarbonylamino group, aminocarbonylamino group, alkylsulfonylamino group,

arylsulfonylamino group, and carbamoyl group, more preferably halogen atom, alkyl group, acylamino group, and alkylsulfonylamino group.

In the formula (B-7), R_{115} represents halogen atom, alkyl group, aryl group, hetero-ring group, nitro group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkoxycarbonylamino group, aminocarbonylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, hetero-ring thio group, alkoxycarbonyl group or carbamoyl group; "x" represents an integer of 0 to 6. Provided that "x" is a plural number, the R_{115} groups in the number "x" may be the same or different. R_{115} is preferably halogen atom, acylamino group, alkoxycarbonylamino group, aminocarbonylamino group, alkylsulfonylamino group, arylsulfonylamino group, and carbamoyl group, more preferably acylamino group, alkylsulfonylamino group, and carbamoyl group.

In the formulas (B-8) and (B-9), R_{116}, R_{117}, R_{118}, and R_{119} independently represents alkyl group or aryl group, and these groups are preferably the same to each other.

In the formula (B-10), R_{120} and R_{121} independently represent alkyl group, aryl group, hetero-ring group, cyano group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, or carbamoyl group; R_{122} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, acylamino group, alkylsulfonylamino group, or arylsulfonylamino group. Preferably, R_{120} and R_{121} are alkyl group, aryl group, hetero-ring group, and cyano group. Preferably, R_{122} is hydrogen atom, alkyl group, aryl group, acylamino group, and alkylsulfonylamino group.

In the formula (B-11), R_{123} and R_{124} independently represent alkyl group, aryl group, hetero-ring group, cyano group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, or carbamoyl group; Z_4 represents a

non-metal atomic group forming a 5-membered or 6-membered ring, together with the two nitrogen atoms and the one carbon atom to which it is attached. R_{125} represents alkyl group, aryl group, alkoxy group, amino group, acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, acyl group, alkoxycarbonyl group, or carbamoyl group; "y" represents an integer of 0 to 2, provided that Z_4 forms a 5-membered ring; and "y" represents an integer of 0 to 3, provided that Z_4 forms a 6-membered ring. Preferably, R_{123} is alkyl group, aryl group, hetero-ring group, and cyano group. Preferably, R_{124} is alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, and carbamoyl group. R_{125} is preferably alkyl group, aryl group, alkylthio group, amino group, and acylamino group.

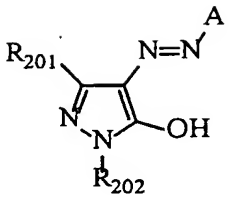
In the formula (B-12), R_{126} represents an alkyl, aryl group, cyano group or alkoxy carbonyl group.

In the formulas (B-1) to (B-12), the preferred number of carbon atoms and specific examples of the individual groups listed in the descriptions of the groups represented by R_{101} to R_{126} are the same as those listed in the description of the substituent for the phenyl or naphthyl group represented by A. Also the heteroatom containing groups have the same meaning as outlined above.

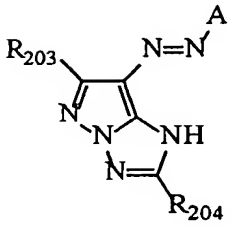
In case that R_{101} to R_{126} in the formulas (B-1) to (B-12) are groups with a possibility of additional substitution, R_{101} to R_{126} may further have a substituent, and the substituent in that case is the same as the substituent listed for the phenyl or naphthyl group represented by A.

Dyes represented by the following formulas DS-1 to DS-9 among compounds represented by the general formula (1) are particularly preferable. "A" in the general formulas DS-1 to DS-9 represents a group with the same meaning as that of "A" in the general formula (1).

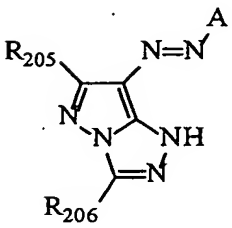
DS-1



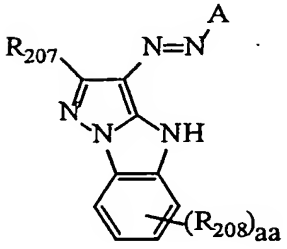
DS-2



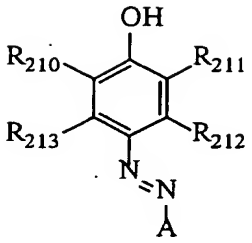
DS-3



DS-4



DS-5



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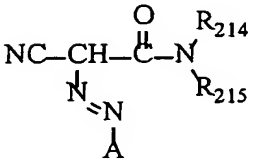

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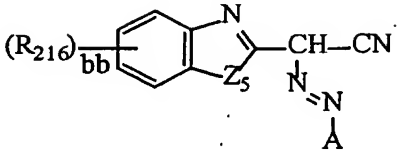
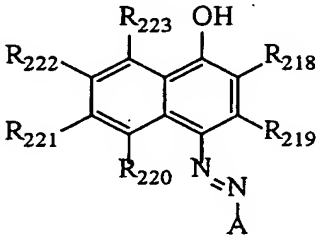


DS-8



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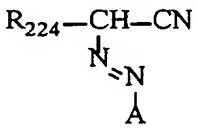


wherein "A" represents a group with the same meaning as defined with respect to the general formula (1).

In the formula DS-1, R_{201} represents hydrogen atom, alkyl group, aryl group, alkoxy group, amino group (including anilino group), alkoxycarbonyl group, cyano group, acylamino group, or carbamoyl group; R_{202} represents hydrogen atom, alkyl group, aryl group, or hetero-ring group. Preferably, R_{201} is alkoxycarbonyl group, cyano group, and carbamoyl group and R_{202} is alkyl group and aryl group.

In the formula DS-2, R_{203} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; R_{204} represents alkyl group, aryl group, or hetero-ring group. R_{203} is preferably hydrogen atom and alkyl group, and the alkyl group particularly preferably includes methyl group, ethyl group, isopropyl group, and t-butyl group. R_{204} is most preferably alkyl group.

In the formula DS-3, R_{205} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; R_{206} represents alkyl group, aryl group, hetero-ring group, alkylthio group, arylthio group, alkoxycarbonyl group, or carbamoyl group. R_{205} is preferably hydrogen atom and alkyl group, and the alkyl group particularly preferably includes methyl group, ethyl group, isopropyl group, and t-butyl group. R_{206} is preferably alkyl group, aryl group, or alkylthio group, most preferably alkyl group.

In the formula DS-4, R_{207} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group,

alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; R_{208} represents halogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, , alkoxycarbonyl group, or carbamoyl group; "aa " represents an integer of 0 to 4; provided that when "aa" is 2 to 4, the R_{208} groups may be same or different. Preferably, R_{207} is hydrogen atom and alkyl group, and the alkyl group particularly preferably includes methyl group, ethyl group, isopropyl group, and t-butyl group. R_{208} is preferably halogen atom, alkyl group, alkoxy group, acylamino group, and alkylsulfonylamino group.

In the formula DS-5, R_{210} and R_{211} independently represent hydrogen atom, halogen atom, alkyl group, aryl group, acylamino group, alkoxycarbonyl group, aminocarbonylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkoxycarbonyl group, or carbamoyl group; R_{212} and R_{213} independently represent hydrogen atom, halogen atom, alkyl group, alkoxy group, or acylamino group. R_{210} and R_{211} preferably represent hydrogen atom, chlorine atom, bromine atom, alkyl group, and acylamino group. R_{212} and R_{213} preferably independently represent hydrogen atom, chlorine atom, bromine atom, alkyl group, and acylamino group. More specifically, at least one of R_{212} and R_{213} is hydrogen atom.

In the formula DS-6, R_{214} and R_{215} independently represent hydrogen atom, alkyl group, aryl group, or hetero-ring group, and one of R_{214} and R_{215} is preferably hydrogen atom.

In the formula DS-7, R_{216} represents halogen atom, alkyl group, aryl group, hetero-ring group, cyano group, alkoxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, sulfamoyl group, alkylsulfonyl group, or carbamoyl group; Z_5 represents oxygen

atom, sulfur atom, or -N(R_{217})-, where R_{217} represents hydrogen atom, alkyl group, aryl group, or hetero-ring group. "bb" represents an integer of 0 to 4. Provided that "bb" is a plural number, the R_{216} groups in the number "bb" may be the same or different. R_{216} is preferably halogen atom, acylamino group, alkylsulfonylamino group, sulfamoyl group, and carbamoyl group. Preferably, Z_5 is oxygen atom, sulfur atom, and -N(R_{217})-, where R_{217} is alkyl group. More preferably, Z_5 is oxygen atom and sulfur atom.

In the formula DS-8, R_{218} represents hydrogen atom, halogen atom, alkyl group, aryl group, acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkoxycarbonyl group, aminocarbonylamino group, carbamoyl group, or sulfamoyl group; R_{220} and R_{223} independently represent hydrogen atom, halogen atom, acylamino group, alkoxycarbonylamino group, aminocarbonylamino group, alkylsulfonylamino group, or arylsulfonylamino group; R_{219}, R_{221}, and R_{222} independently represent hydrogen atom, chlorine atom, bromine atom, alkyl group, or acylamino group. R_{218} is preferably hydrogen atom, acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkoxycarbonyl group, aminocarbonylamino group, carbamoyl group, and sulfamoyl group. R_{220} and R_{223} are preferably independently hydrogen atom, acylamino group, alkoxycarbonylamino group, and alkylsulfonylamino group. R_{219}, R_{221}, and R_{222} are preferably hydrogen atom.

In the formula DS-9, R_{224} represents an alkyl, aryl group cyano group or alkoxy carbonyl group.

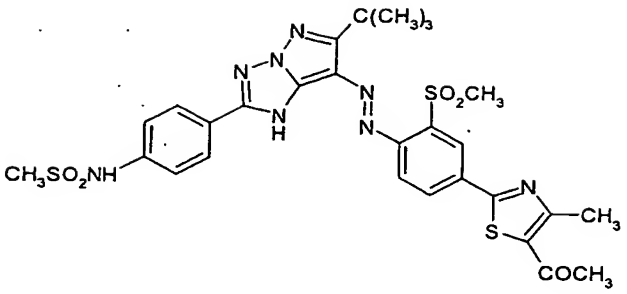
In the formulas DS-1 to DS-9, preferable carbon numbers and specific examples of the individual groups listed in the descriptions of the groups represented by R_{201} to R_{224} are the same as those listed in the description of the substituent for the phenyl or naphthyl group represented by "A".

Provided that R_{201} to R_{224} in the formulas DS-1 to DS-9 are groups with a possibility of additional substitution, R_{201}

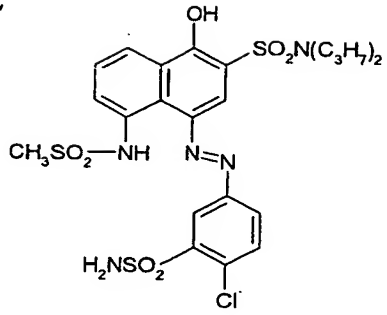
to R_{224} may have additional substituents. The substituents then are the same as those listed in the description of the substituent for the hetero-ring group represented by "A".

Specific compound examples of the dissociative azo dyes represented by the general formula (1) in accordance with the invention are described below, but the invention is not limited to these examples.

D-1



D-2



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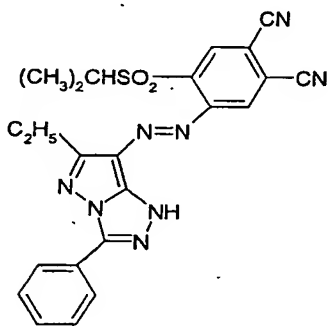

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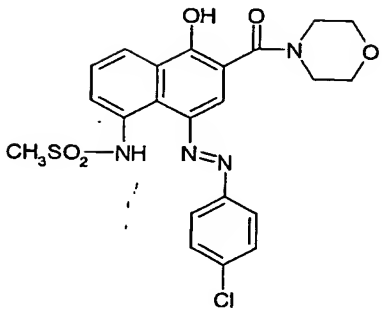

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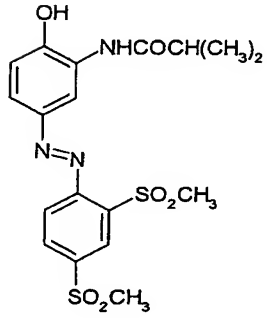
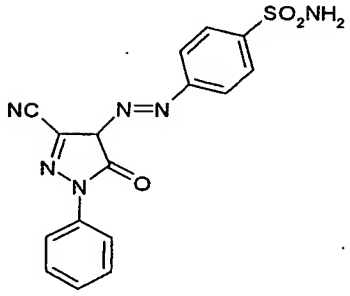


D-6



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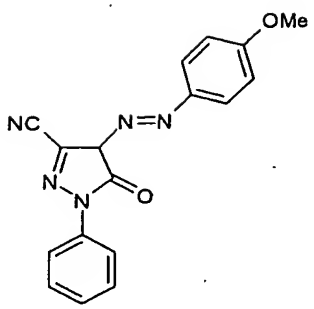
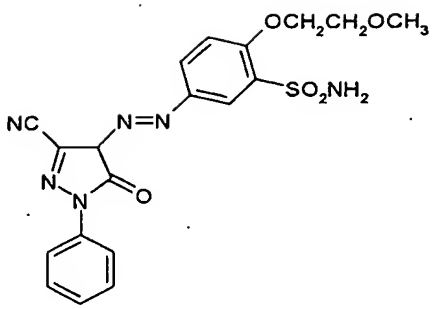
D-7



D-8



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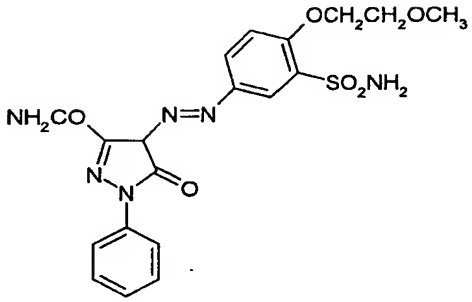
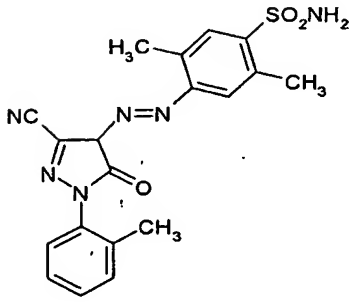


D-10



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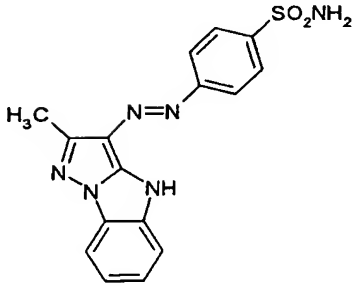

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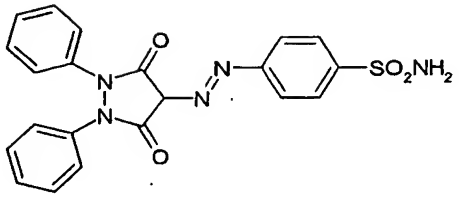

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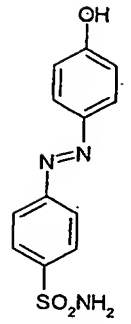
D-13



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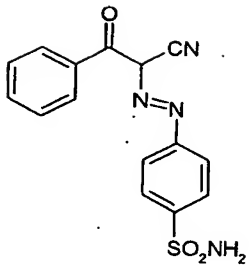

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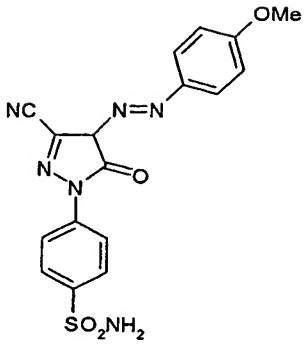

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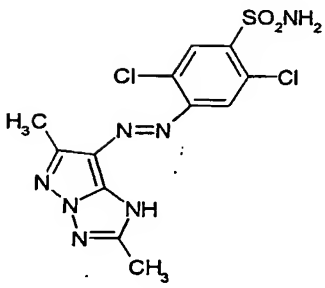
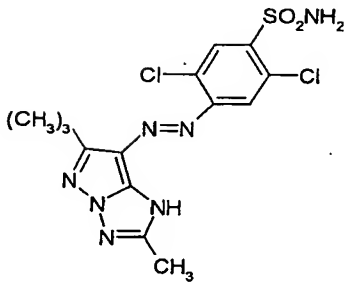
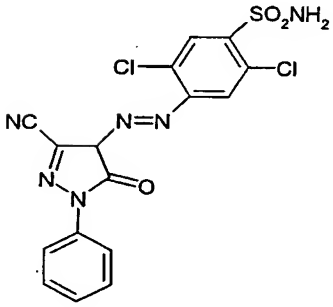


D-17



D-18



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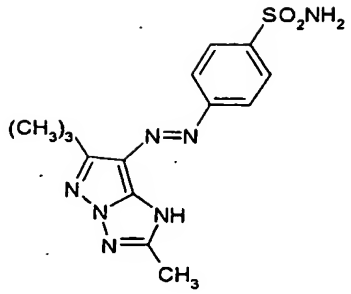
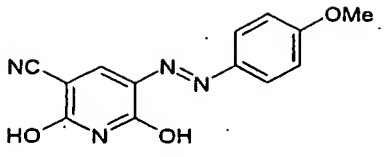
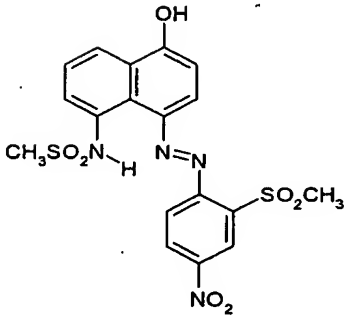
D-19



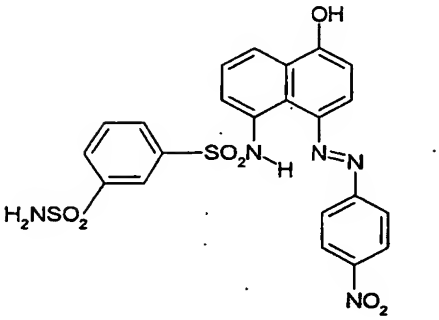
D-20



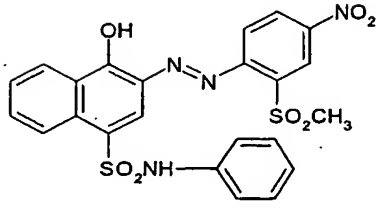
D-21



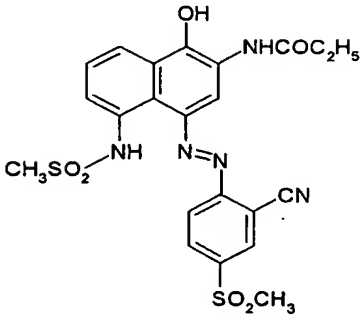
D-22



D-23



D-24



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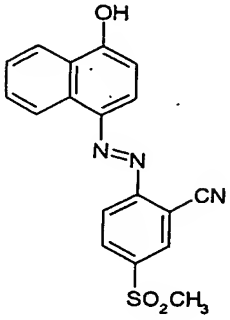
D-25



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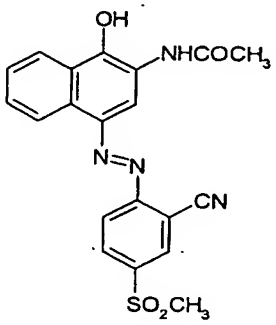

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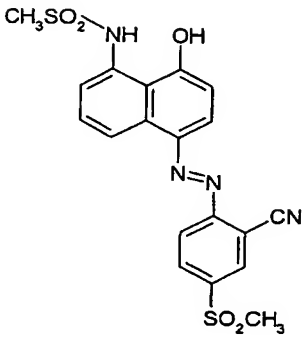

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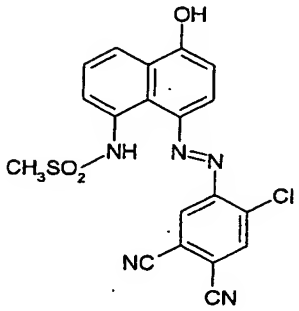
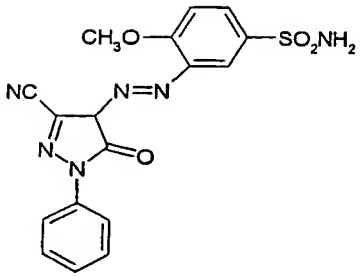


D-29



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In the present invention, dissociative dyes are to be understood to mean those dyes that contain at least one group having a pKa value preferably falling within the range 1.5 to 9, more preferably 2 to 8 and most preferably 2 to 7.5. It is most preferred that the dissociative dyes do not contain any groups having a pKa value below 1.5. The pKa of the azo dyes is one possibility for determining the dyeing power of the dyes. The groups having a pKa value of from 1.5 to 9 are for example phenolic OH-groups, CH-acidic groups (active methylene, active methine), -NH-groups in conjugated heterocyclic rings, OH-groups attached to the conjugated heterocyclic rings and the like.

The pKa value is determined in DMF/water (1/1-mixture, by volume) as follows:

The dye is dissolved in a solution of a DMF/water (1/1; volume ratio) to a final concentration of 2×10^{-5} mol/l. After the resulting solution is adjusted to pH 2, using 1.0 mol/l hydrochloric acid, the solution is titrated with aqueous 1.0 mol/l sodium hydroxide solution. Recording the change of the visible ultra-violet absorption spectrum, the inflection point is determined by regression analysis.

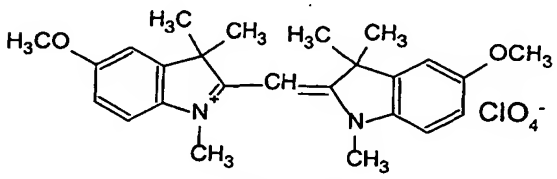
The dissociative azo dye represented by the formula (I) has a dissociative proton in the chromophore of the dye. The hue of the dye in an aqueous medium may change at a higher pH due to the dissociation of the proton and the formation of the anionic dye.

In another aspect of the present invention, there is also provided a hair dyeing method comprising applying the above-described hair dye composition to the hair.

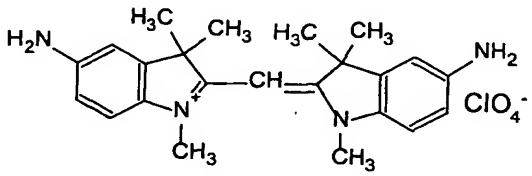
One or more of the above mentioned, particularly preferred azo direct dyes (D-1 to D-24) can be used. Additionally, it may be used in combination with another direct dye or with oxidative dyes.

Examples of additional direct dyes that can be used in combination with the direct dyes of the invention include,

Basic Blue 7 (C.I. 42595), Basic Blue 26 (C.I. 44045), Basic Blue 99 (C.I. 56059), Basic Violet 10 (C.I. 45170), Basic Violet 14 (C.I. 42515), Basic Brown 16 (C.I. 12250), Basic Brown 17 (C.I. 12251), Basic Red 2 (C.I. 50240), Basic Red 12 (C.I. 48070), Basic Red 22 (C.I. 11055), Basic Red 46 (C.I. 110825), Basic Red 76 (C.I. 12245), Basic Red 118 (C.I. 12251:1), Basic Yellow 28 (C.I. 48054) and Basic Yellow 57 (C.I. 12719); cationic dyes as described in Japanese Patent Publication No. Sho 58-2204, Japanese Patent Application Laid-Open (*kokai*) No. Hei 9-118832, Japanese Patent Laid-Open Publications (PCT) Nos. Hei 8-501322 and Hei 8-507545; and methine type cationic dyes having a cyanine structure represented by the below-described formulas.



Yellow dye



Orange dye

The azo dyes represented by the formula (I) are preferably added in an amount of 0.0001 to 20 wt.%, more preferably 0.001 to 20 wt.%, further preferably 0.05 to 10 wt.%, especially 0.1 to 5 wt.% based on the whole composition (after mixing of all the component parts when the composition is a two part or three part composition; this will be applied equally hereinafter). When another direct dye is used in combination, the total amount of this dye together with the direct dye (I) is 0.001 to 20 wt.%, preferably 0.01 to 20 wt.%, more preferably in the range from 0.05 to 10 wt.%, especially 0.1 to 5 wt.%, based on the whole composition.

In the hair dye composition of the present invention, the direct dye (I) exhibits high storage stability within a

wide pH range from 2 to 11 which is a pH range employed ordinarily for hair dyes, so that the hair dye composition can be used freely in the above-described pH range. Use in a pH range of 5 or greater is however preferred from the viewpoint of dyeing property. Moreover, owing to high stability of the direct dye against an alkaline agent, the hair dye composition can be used at a pH above 8, particularly 8 to 11 which permits a high dyeing power, and even after storage for a long period of time, it exhibits high dyeing power without decomposition of the direct dye. Examples of the alkaline agent that may be used in the dyeing composition include ammonia, alkanolamines such as monoethanolamine and isopropanolamine or salts thereof, guanidium salts such as guanidine carbonate and hydroxide salts such as sodium hydroxide. The alkaline agent is preferably added in an amount of 0.01 to 20 wt.%, more preferably 0.1 to 10 wt.%, especially 0.5 to 5 wt.% based on the whole composition.

Since in the hair dye composition of the present invention, the direct dye (I) has high stability against an oxidizing agent, it can be applied to the hair after mixing with an oxidizing agent. In other words, it can be provided in the form composed of a first component part containing the direct dye (I) and a second component part containing an oxidizing agent. In this case, hair dyeing and bleaching can be carried out simultaneously, which facilitates more vivid hair dyeing. Examples of the oxidizing agent include hydrogen peroxide, persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate, perborates such as sodium perborate, percarbonates such as sodium percarbonate and bromates such as sodium bromate and potassium bromate. Hydrogen peroxide is especially preferred for hair bleaching property, stability of the dye and availability. It is also preferred to use a combination of hydrogen peroxide with at least one of the above mentioned

other oxidizing agents. The oxidizing agent is preferably added in an amount of 0.5 to 10 wt.%, especially 1 to 8 wt.%, based on the whole composition. The mixing ratio of the first component part containing the direct dye (I) with the oxidizing-agent-containing second component part preferably ranges from 2:1 to 1:3 in terms of a volume ratio.

In the hair dye composition of the present invention, the direct dye (I) can also be used in combination with one or more oxidation dyes. The combined use attains a markedly more vivid and stronger colour which is not possible by the use of an oxidation dye alone. For the oxidation dye, known developers and couplers ordinarily employed for an oxidation type hair dye can be used.

Examples of the developer include paraphenylenediamine, toluene-2,5-diamine, 2-chloro-paraphenylenediamine, N-methoxyethyl-paraphenylenediamine, N,N-bis(2-hydroxyethyl)-paraphenylenediamine, 2-(2-hydroxyethyl)-paraphenylenediamine, 2,6-dimethylpara-phenylenediamine, 4,4'-diaminodiphenylamine, 1,3-bis(N-(2-hydroxyethyl)-N-(4-aminophenyl)amino)-2-propanol, PEG-3,2,2'-paraphenylenediamine, paraaminophenol, paramethylaminophenol, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 2-(2-hydroxyethylaminomethyl)-4-aminophenol, orthoaminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-acetamidophenol, 3,4-diaminobenzoic acid, 5-aminosalicylic acid, 2,4,5,6-tetraaminopyrimidine, 2,5,6-triamino-4-hydroxypyrimidine and 4,5-diamino-1-(4'-chlorobenzyl)pyrazole and salts thereof.

Examples of the coupler include metaphenylenediamine, 2,4-diaminophenoxyethanol, 2-amino-4-(2-hydroxyethylamino)anisole, 2,4-diamino-5-methylphenetole, 2,4-diamino-5-(2-hydroxyethoxy)toluene, 2,4-dimethoxy-1,3-diaminobenzene, 2,6-bis(2-hydroxyethylaminotoluene, 2,4-diamino-5-fluorotoluene, 1,3-bis(2,4-diaminophenoxy)propane, metaaminophenol, 2-methyl-5-aminophenol, 2-methyl-5-(2-

hydroxyethylamino)phenol, 2,4-dichloro-3-aminophenol, 2-chloro-3-amino-6-methylphenol, 2-methyl-4-chloro-5-aminophenol, N-cyclopentyl-metaaminophenol, 2-methyl-4-methoxy-5-(2-hydroxyethylamino)phenol, 2-methyl-4-fluoro-5-aminophenol, resorcin, 2-methylresorcin, 4-chlororesorcin, 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2-isopropyl-5-methylphenol, 4-hydroxyindole, 5-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole, 6-hydroxybenzomorpholine, 3,4-methylenedioxyphenol, 2-bromo-4,5-methylenedioxyphenol, 3,4-methylenedioxyaniline, 1-(2-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-diaminopyridine, 2,3-diamino-6-methoxypyridine, 2-methylamino-3-amino-6-methoxypyridine, 2-amino-3-hydroxypyridine, and 2,6-diaminopyridine and salts thereof.

At least one of the above-exemplified ones can be used as the developer and coupler. The amount of each of the developer and coupler is preferably 0.01 to 20 wt.%, especially 0.5 to 10 wt.% each based on the whole composition.

To the hair dye composition of the present invention, a known autoxidation dye typified by an indole or an indoline, or a known direct dye such as a nitro dye or a disperse dye can also be added.

Addition of a polyol, polyol alkyl ether, cationic or amphoteric polymer or silicone to the hair dye composition of the present invention is preferred, because the resulting composition can dye the hair uniformly and has improved cosmetic effects of the hair.

In addition to the above-described components, those ordinarily employed as a raw material for cosmetics can be added to the hair dye composition of the present invention. Examples of such an optional component include hydrocarbons, animal or vegetable fats and oils, higher fatty acids,

organic solvents, penetration promoters, cationic surfactants, natural or synthetic polymers, higher alcohols, ethers, amphoteric surfactants, nonionic surfactants, anionic surfactants, protein derivatives, amino acids, antiseptics, chelating agents, stabilizing agents, antioxidants, plant extracts, crude drug extracts, vitamins, colourants, perfumes and ultraviolet absorbers.

The hair dye composition of the present invention can be prepared in a conventional manner into a one-part composition, a two-part composition having a first component part containing an alkaline agent and a second component part containing an oxidizing agent, or a three-part composition having, in addition to these two component parts, a powdery oxidizing agent such as persulfate. The direct dye (I) may be incorporated in either one or both of these component parts of the two-part or three-part composition. When the hair dye composition of the present invention is one-part type, it is applied to the hair directly, while the two- or three-part type is applied to the hair after mixing these parts upon hair dyeing.

Typically, the first composition comprises the azo dye represented by the formula (I) and an alkaline agent in an aqueous medium with a pH of from 8 to 12. The second composition comprises hydrogen peroxide in a slightly acidic aqueous medium. The third composition comprises a persulfate and inert powder to form agglomerates. Small amounts of the third composition are added into the mixture of the first and the second composition.

No particular limitation is imposed on the form of the hair dye composition of the present invention. Examples include powder, transparent liquid, emulsion, cream, gel, paste, aerosol, and aerosol foam. It preferably has a viscosity of 2000 to 100000 mPa·s in the stage of application to the hair (after mixing of all the component parts when the composition is a two-part or three-part type). The viscosity

is measured at 20°C by using a Brookfield rotary viscosimeter with a spindle No. 5 at 5 rpm.

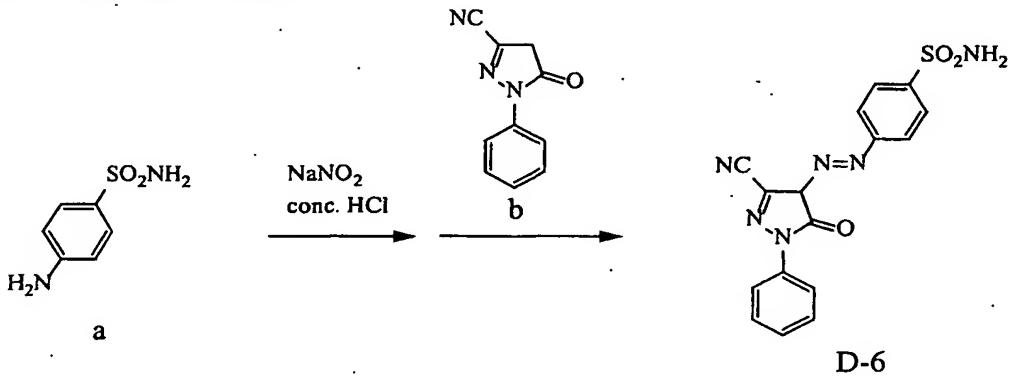
Examples

The present invention will be described in greater detail by referring to the examples and comparative examples.

Specific synthetic examples of the compound represented by the general formula (1) in accordance with the invention will be described below.

Synthesis of listed compound D-6

The compound was synthetically prepared according to the following scheme.



Sulfanilamide (intermediate a, 25.8g; 0.150mol) and conc. hydrochloric acid (45.0 ml; 0.525 mol) were added to 150 ml of water, and the resulting mixture was stirred for 30 min under cooling in ice water bath. Sodium nitrite solution (10.4 g; 0.150 mol in 20 ml of water) was added dropwise over 20 min. The resulting mixture was stirred for 1 hr under cooling in ice water bath.

3-Cyano-1-phenyl-5-pyrazolone (intermediate b, 27.8g; 0.150 mol) were added to 200 ml of methanol. After stirring for a few minutes, sodium acetate (43.1 g; 0.525 mol) and 50 ml of water was added to the mixture and the resulting mixture was stirred under cooling in ice water bath for 20

min. To this mixture, the diazonium salt solution prepared above was added gradually over 1hr. After stirring under cooling for one and half hours , the precipitate was filtered off and washed with water, dried to 55.2 g of the crude product of D-6.

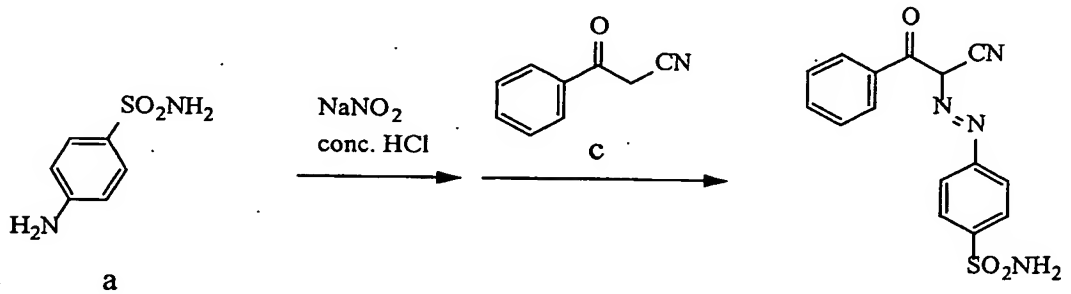
The crude product and triethylamine (20.9 ml; 0.150 mol) were added to 260 ml of methanol and the resulting mixture was refluxed for 20 min with stirring. After short cooling to stop refluxing, the hot mixture was filtered through Celite pad and washed with 50 ml of methanol. The filtrate was stirring under cooling in water bath. To the mixture, diluted hydrochloric acid (12.8 ml of conc. hydrochloric acid was diluted with 25 ml of water) was added dropwise over about 20 min. After stirring for 1hr, the precipitate was filtered off and washed with 140 ml of methanol. The wet cake of D-6 was added to 200 ml of acetonitrile and the resulting mixture was refluxed for 30 min with stirring. After cooled to room temperature with stirring, the precipitate was filtered off, washed with 80 ml of acetonitrile, dried to 50.6 g of D-6 as orange crystal (91.6%)

^{1}H NMR (DMSO-d_6, ppm)

7.95-7.85 (m, 6H), 7.53 (t, 2H), 7.42 (brs, 2H), 7.35 (t, 1H)

Synthesis of listed compound D-14

The compound was synthetically prepared according to the following scheme.



a

D-14

Sulfanilamide (intermediate a, 25.8g; 0.150mol) and conc. hydrochloric acid (45.0 ml; 0.525 mol) were added to 150 ml of water, and the resulting mixture was stirred for 30 min under cooling in ice water bath. Sodium nitrite solution (10.4 g; 0.150 mol in 20 ml of water) was added dropwise over 20 min. The resulting mixture was stirred for 1 hr under cooling in ice water bath.

Benzoylacetonitrile (intermediate c, 21.8g; 0.150 mol) were added to 200 ml of methanol. After stirring for a few min, sodium acetate (43.1 g; 0.525 mol) and 50 ml of water was added to the mixture and the resulting mixture was stirred under cooling in ice water bath for 20 min. To this mixture, the diazonium salt solution prepared above was added gradually over 1hr. After stirring under cooling for one and half hrs, the precipitate was filtered off and washed with water, dried to 47.7 g of the crude product of D-14.

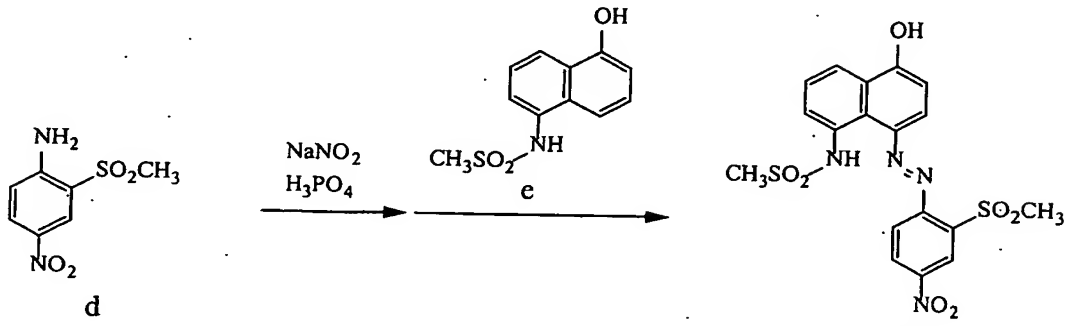
The crude product and triethylamine (24.3 ml; 0.174 mol) were added to 250 ml of methanol and the resulting mixture was refluxed for 20 min with stirring. After short cooling to stop refluxing, the hot mixture was filtered through Celite pad and washed with 50 ml of methanol. To the stirring filtrate under cooling in water bath, diluted hydrochloric acid (15.0 ml of conc. hydrochloric acid was diluted with 30 ml of water) was added dropwise over about 30 min. After stirring for 1hr, the precipitate was filtered off, washed with 100 ml of methanol and 100 ml of water. The wet cake of D-14 was added to 150 ml of acetonitrile and the resulting mixture was refluxed for 30 min with stirring. After cooled to room temperature with stirring, the precipitate was filtered off, washed with 100 ml of acetonitrile, dried to 46.7 g of D-14 as yellow crystal (94.8%).

^{1}H NMR (DMSO-d_6, ppm)

12.53 (brs, 1H), 7.90 (dd, 2H), 7.81 (d, 2H), 7.66 (t, 1H), 7.56 (t, 2H), 7.48 (d, 2H), 7.30 (brs, 2H)

Synthesis of listed compound D-21

The compound was synthetically prepared according to the following scheme.



2-Methylsulfonyl-4-nitroaniline (intermediate d, 13.0 g; 60.0 mmol) was added to 50 ml of phosphoric acid, and the resulting mixture was vigorously stirred under cooling in ice water. Sodium nitrite (4.00 g; 58.0 mmol) in crystal was added to the mixture, which was stirred for 1 hr.

5-Methylsulfonylamino-1-naphthol (intermediate e, 11.9g; 50.0 mmol) was added to methanol (100 ml), and the resulting mixture was stirred under cooling in ice water bath, to which was then gradually added the diazo solution prepared above in a divided manner over 30 min. The temperature of the reaction mixture was maintained under 10°C . After stirring under cooling for one hr and stirring at room temperature for another hr, 100 ml of water was added dropwise to the reaction mixture. After stirring for 30 min, the precipitate was filtered off, washed with 150 ml of water. After dried overnight at about 40°C , the crude product of D-21 was obtained (24.7 g).

The crude product and triethylamine (16.8 ml; 0.120 mol) were added to 400 ml of methanol and the resulting mixture was refluxed for 40 min with stirring. After short cooling to stop refluxing, the hot mixture was filtered through Celite pad and washed with 100 ml of methanol. To the stirring filtrate under cooling in water bath, diluted hydrochloric

acid (10.4 ml of conc. hydrochloric acid was diluted with 30 ml of water) was added dropwise over about 30 min. After stirring for 30 min, the precipitate was filtered off, washed with 100 ml of methanol. The wet cake of D-21 was added to 100 ml of acetonitrile and the resulting mixture was refluxed for 30 min with stirring. After cooled to room temperature with stirring, the precipitate was filtered off, washed with 50 ml of acetonitrile, dried to 10.5 g of D-21 (45.2%).

^{1}H NMR (DMSO-d_6, ppm)

12.8 (brs, 1H), 8.60 (d, 1H), 7.42 (brs, 1H), 8.20 (brd, 1H), 7.92 (d, 1H), 7.83 (d, 1H), 7.71 (d, 1H), 7.51 (t, 1H), 6.72 (brd, 1H), 3.49 (s, 3H), 3.20 (s. 3H)

1) Examples of Dyeing Performance of Dyestuffs

The dyes listed in Tables 1a and 1b were dissolved into a mainly aqueous formulation containing alkaline peroxide and applied in the form of a composition having the General Formulation A to goat and human hair.

General Formulation A

Dyestuff of formula (I)	0.2g
Benzyl Alcolohol	5.0g
Sodium Lauryl Sulphate	0.01g
Ammonium Hydroxide (25%)	5.0g
Hydrogen Peroxide (50%)	6.0g
Water	up to 100g
pH	10.0

The dye mixture was applied to undamaged white goat hair and to undamaged human blond hair at 50°C for 15mins. 1.5-2.0g of General Formulation A was applied per gram of hair. After the dyeing time (approximately 15 to 30 minutes) was complete, the tresses were rinsed with water, shampoo washed and then dried. The color of the tresses was then recorded. L, a and b values of the tresses before and after the colouring treatment were measured by Minolta colour-measuring

instrument and the value of delta E, which is a known measure for the chroma, was calculated according to the well-known equation: $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$ for each example (this will apply equally to every example hereinafter). The results are shown in Table 1a (Goat Hair) and Table 1b (Human Hair.)

Table 1a: Color on Undamaged White Goat Hair

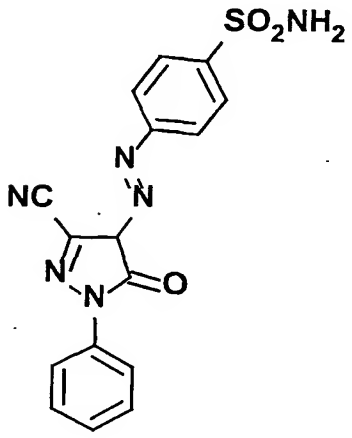
Dye Example	Color of Dyed Hair	L	a	b	Delta E
D-2	Bright Pink/Magenta	51	44	-10	60
D-4	Intense Pink	48	51	-2	65
D-5	Pink	48	42	-2	58
D-6	Bright Yellow	81	0	72	58
D-7	Intense Gold	76	14	74	62
D-8	Bright Yellow	84	-3	63	49
D-9	Bright Yellow	83	-2	57	44
D-10	Bright Gold Yellow	79	3	68	54
D-14	Intense Yellow	84	-11	65	52
D-15	Orange/Gold	76	13	62	50
D-16	Bright Yellow	82	1	66	52
D-17	Bright Gold	78	7	71	57
D-18	Yellow-Orange	75	18	66	56
D-19	Intense Yellow	82	-4	66	52
D-21	Intense Cyan	37	-17	-18	60
D-22	Cyan	44	-4	-4	45
D-23	Blue	44	9	-22	56
D-24	Cyan	56	-11	-16	44
D-25	Ash Blue	38	8	-5	51
D-27	Bright Blue	37	10	-26	63
D-29	Bright Yellow	80	3	70	56

Table 1b: Color on Undamaged Human Blonde Hair

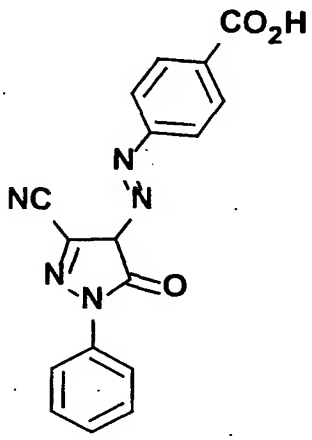
Dye Example	Color of Dyed Hair	L	a	b	Delta E
D-2	Pink/Red	39	21	8	18
D-4	Pink	33	31	9	28
D-5	Light Pink	42	21	12	17
D-6	Bright Yellow	57	7	41	26
D-7	Intense Gold	53	10	44	28
D-8	Bright Yellow	58	6	30	18
D-9	Bright Yellow	56	6	30	16
D-10	Bright Gold Yellow	56	6	36	22
D-14	Intense Yellow	56	4	35	21
D-15	Orange/Gold	54	9	36	21
D-16	Bright Yellow	60	3	19	25
D-17	Bright Gold	56	6	36	22
D-18	Yellow-Orange	62	6	34	23
D-19	Intense Yellow	64	4	26	20
D-21	Intense Cyan	35	-18	-4	33
D-22	Olive Brown	36	-2	7	15
D-23	Ash Blue	36	2	1	17
D-24	Olive Brown	43	-6	7	16
D-25	Ash Blue	34	6	9	11
D-27	Blue	32	2	-4	23
D-29	Bright Yellow	54	7	35	20

2) Comparison with anionic dyes

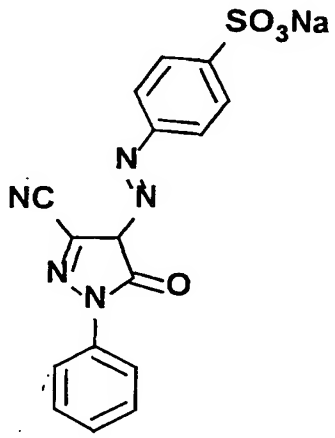
The performance of dyes of the invention were compared with that of dyes not covered by the invention. Thus dyes D-6, A* and B* were used within general Formulation A and applied to undamaged white goat hair and undamaged human blonde hair for 15mins at 50°C (see Tables 2a and 2b.)



(D-6)



(A)*



(B)*

Table 2a: Color uptake on undamaged white goat hair

Dye	Color	L	a	b	Delta E
(D-6)	Very Intense Yellow	81	0	72	59
(A)*	Pale Yellow	86	-6	41	42
(B)*	Pale Yellow	85	-5	42	43

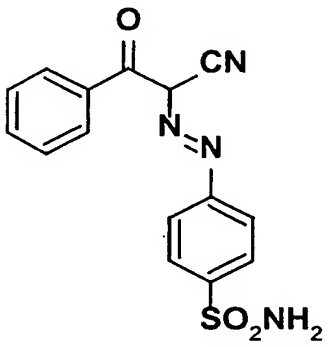
* Not according to the invention

Table 2b: Color uptake undamaged Blonde human hair

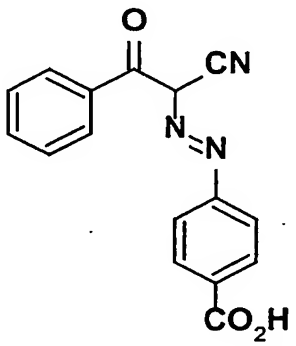
Dye	Color	L	a	b	Delta E
(D-6)	Very Intense Gold	57	7	41	**26**
(A)*	Pale Yellow	55	7	26	13
(B)*	Pale Yellow	55	6	26	13

* Not according to the invention

Furthermore a comparison of the dyeing performance of dyes D-14 and C* was carried out using General Formulation A and the same dyeing method as described above. The results are shown in Tables 3a and 3b.



(D-14)



(C *)

Table 3a: Color uptake on undamaged white goat hair

Dye	Color	L	a	b	Delta E
(D-14)	Very Intense Yellow	84	-11	65	**52**
(C)*	Pale Yellow	87	-6	31	19

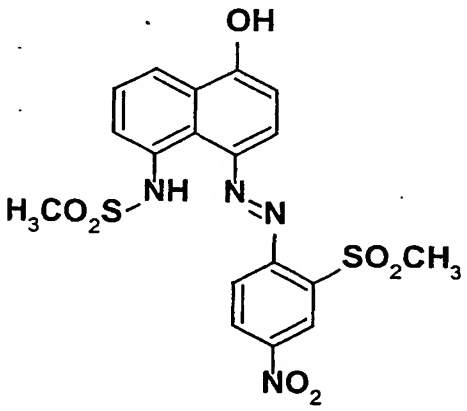
* Not according to the invention

Table 3b: Color uptake undamaged Blonde human hair

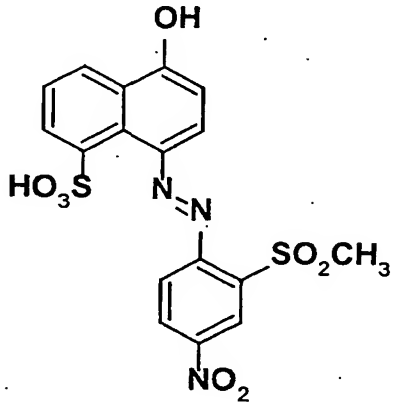
Dye	Color	L	a	B	Delta E
(D-14)	Very Intense Gold	56	4	35	**21**
(C)*	Pale Yellow	52	6	25	12

* Not according to the invention

Similarly, the performance of (D-21) and (D)* were also compared in General Formulation A. The results are summarised in Tables 4a and 4b.



(D-21)



(D)*

Table 4a: Color uptake on undamaged white goat hair

Dye	Color	L	a	B	Delta E
(D-21)	Intense Cyan	37	-17	-18	**60**
(D)*	Pale Cyan	65	-13	2	23

* Not according to the invention

Table 4b: Color uptake on undamaged Blonde human hair

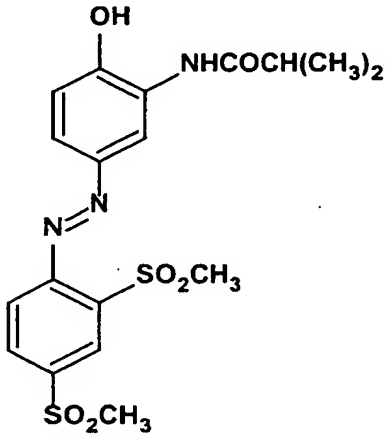
Dye	Color	L	a	B	Delta E
(D-21)	Intense Cyan	35	18	-4	33
(D)*	Pale Blonde	51	2	19	7

* Not according to the invention

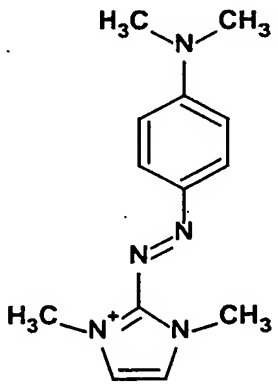
In all cases, the dyes containing sulfo or carboxylic groups provided much weaker color on hair than the analogous non-anionic dyestuff. Clearly, the presence of a -COOH or a $-SO_3H$ group, drastically reduces dyeing performance and thus these groups are excluded from the invention.

3) Examples of wash fade.

In order to assess the performance of the dyes of general formula I as defined, in terms of resistance to fading from washing, Dyes D-37 and D-41 were compared with a diazo dye containing a cationic group (E)*.



D-5



(E)*

* Not according to the invention

Using the same formulation as described above (General Formulation A), the dyes were applied for 15mins at 50°C to damage (permed) white goat hair. After the dyeing process was complete, the tresses were washed and dried and the color noted. The tresses were then put through a wash fade

protocol, to measure the resistance to shampoo washing. The washing protocol consisted of applying 0.1g of shampoo per 1g of hair and milking into the hair for 30 seconds followed by rinsing the tresses for 30seconds with 40°C water. This process was repeated 20 times. The tresses were then dried and the change in color measured as a delta E value, using the Minolta Colorimeter. The results are shown in Table 4.

Table 4: Washfastness of Dye of the Invention compared to Cationic Dyes not of the invention

Dye Example	Treament	L	a	b	Δ E fade
D-5	Initial	33	55	0	
D-5	20 washes	34	57	0	3
Cationic Direct Dye E*	Initial	32	58	19	
Cationic Direct Dye E*	20 Washes	54	58	4	27

* Not according to the invention

Clearly, the presence of a cationic group drastically reduces the durability of the dyestuffs to shampoo washing on damaged hair. Thus, cationic substituents are excluded from the invention.

4) pka values of some illustrated dyes.

The pka values of some dyes in accordance with the present invention have been measured as described in the specification. The values are shown below:

Dyes	pka
D-6	4.2
D-7	4.6
D-14	5.82
D-15	4.36

5	D-17	5.92
	D-18	2.86
	D-21	4.32
	D-22	6.34
	D-24	5.09
10	D-25	6.5
	D-26	7.1

CLAIMS

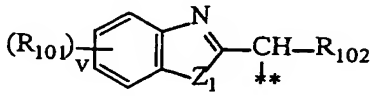
1. Hair dyeing composition comprising a dissociative azo dye represented by the formula (I)

A-N=N-B (I)

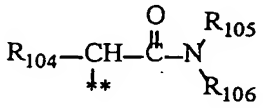
wherein A represents a phenyl or naphthyl group, wherein these groups may be substituted, wherein these phenyl or naphthyl groups do not contain sulfo or carboxyl groups or quaternary ammonium groups; and B represents an aromatic group required for the compound represented by the general formula (I) to form a dissociative azo dye which is free from anionic sulfo or carboxyl groups and quaternary ammonium groups.

2. Hair dyeing composition according to claim 1, wherein B is selected from the following groups (B-1) to (B-12) binding via symbol ** to the azo group:

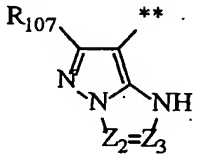
(B-1)



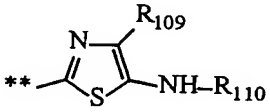
(B-2)



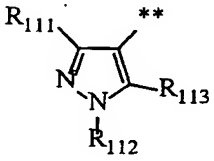
(B-3)



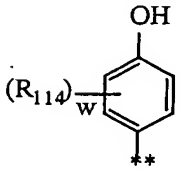
(B-4)



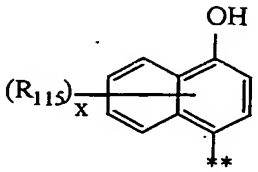
(B-5)



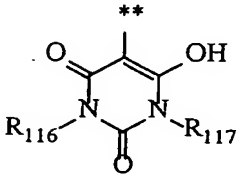
(B-6)



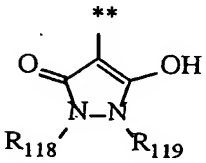
(B-7)



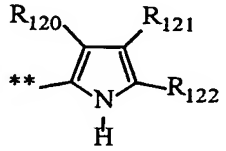
(B-8)



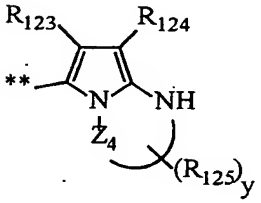
(B-9)



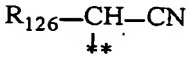
(B-10)



(B-11)



(B-12)



wherein R_{101} represents halogen atom, alkyl group, aryl group, hetero-ring group, cyano group, alkoxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio

group, arylthio group, sulfamoyl group, alkylsulfonyl group, or carbamoyl group, R_{102} and R_{104} each independently represent cyano group, alkylsulfonyl group, arylsulfonyl group, acyl group, alkoxycarbonyl group, aryloxycarbonyl group, or carbamoyl group. Z_1 represents oxygen atom, sulfur atom, or $-N(R_{103})-$, wherein R_{103} represents hydrogen atom, alkyl group, aryl group or hetero-ring group, "v" represents an integer of 0 to 4, wherein several R_{101} groups may be the same or different;

R_{107} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; Z_2 and Z_3 independently represent $-C(R_{108})=$, or $-N=$; R_{108} represents alkyl group, aryl group, hetero-ring group, alkylthio group, arylthio group, alkoxycarbonyl group, or carbamoyl group, wherein if Z_2 and Z_3 both represent $-C(R_{108})=$, two R_{108} groups may be the same or different or may bind together to form a carbon ring or a hetero-ring;

R_{109} represents alkyl group, aryl group or hetero-ring group, and R_{110} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, acyl group, alkylsulfonyl group or arylsulfonyl group,

R_{111} represents hydrogen atom alkyl group, aryl group, alkoxy group, amino group (including anilino group), alkoxycarbonyl group, cyano group, acylamino group, or carbamoyl group; R_{112} represents hydrogen atom, alkyl group, aryl group, or hetero-ring group; R_{113} represents hydroxy group or amino group, R_{114} represents halogen atom, alkyl group, aryl group, hetero-ring group, nitro group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkoxycarbonylamino group, aminocarbonylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio

group, arylthio group, hetero-ring thio group, alkoxycarbonyl group, or carbamoyl group; "w" represents an integer of 0 to 4, wherein several R_{114} groups in the number "w" may be the same or different,

R_{115} has the meanings of R_{114} or is an alkoxy; "x" represents an integer of 0 to 6, wherein several R_{115} groups in the number "x" may be the same or different,

R_{116}, R_{117}, R_{118}, and R_{119} independently represents alkyl group or aryl group, R_{120} and R_{121} independently represents alkyl group, aryl group, hetero-ring group, cyano group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, or carbamoyl group; R_{122} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, acylamino group, alkylsulfonylamino group, or arylsulfonylamino group,

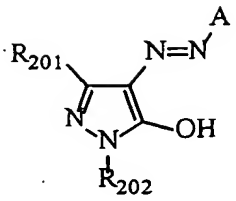
R_{123} and R_{124} independently represents alkyl group, aryl group, hetero-ring group, cyano group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, or carbamoyl group;

Z_4 represents a non-metal atomic group forming a 5-membered or 6-membered ring, together with the two nitrogen atoms and one carbon atom, R_{125} represents alkyl group, aryl group, alkoxy group, amino group, acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, acyl group, alkoxycarbonyl group, or carbamoyl group; "y" represents an integer of 0 to 2, when Z_4 forms a 5-membered ring; and "y" represents an integer of 0 to 3, when Z_4 forms a 6-membered ring, and

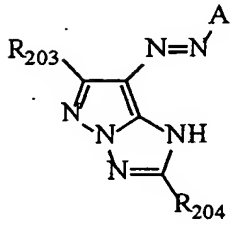
R_{126} represents alkyl group, aryl group, cyano group or alkoxy carbonyl group.

3. Hair dyeing composition according to claim 1 or 2, wherein the structure of the dye is represented by DS-1 to DS-9:

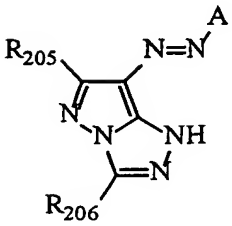
DS-1



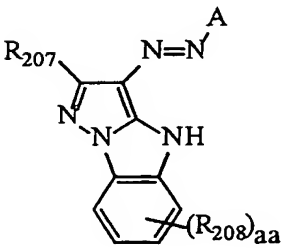
DS-2



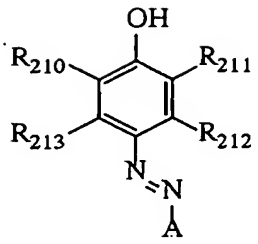
DS-3



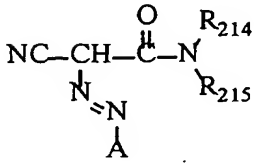
DS-4



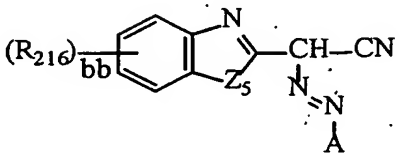
DS-5



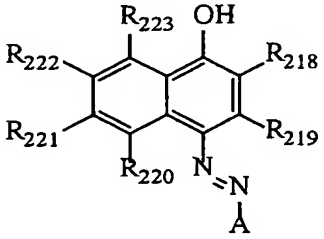
DS-6



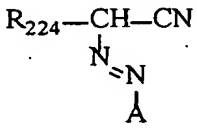
DS-7



DS-8



DS-9



wherein "A" has the same meaning as defined in claim 1;

R_{201} represents hydrogen atom, alkyl group, aryl group, alkoxy group, amino group (including anilino group), alkoxycarbonyl group, cyano group, acylamino group, or carbamoyl group;

R_{202} represents hydrogen atom, alkyl group, aryl group, or hetero-ring group;

R_{203} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; R_{204} represents alkyl group, aryl group, or hetero-ring group;

R_{205} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; R_{206} represents alkyl group, aryl group, hetero-ring group, alkylthio group, arylthio group, alkoxycarbonyl group, or carbamoyl group;

R_{207} represents hydrogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, or carbamoyl group; R_{208} represents halogen atom, alkyl group, aryl group, hetero-ring group, alkoxy group, aryloxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, or carbamoyl group; "aa" represents an integer of 0 to 4, provided that aa is 2 to 4, the R_{208} groups may be the same or different;

R_{210} and R_{211} independently represent hydrogen atom, halogen atom, alkyl group, aryl group, acylamino group, alkoxycarbonyl group, aminocarbonylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkoxycarbonyl group, or carbamoyl group; R_{212} and R_{213}

independently represent hydrogen atom, halogen atom, alkyl group, alkoxy group, or acylamino group;

R_{214} and R_{215} independently represent hydrogen atom, alkyl group, aryl group, or hetero-ring group;

R_{216} represents halogen atom, alkyl group, aryl group, hetero-ring group, cyano group, alkoxy group, amino group (including anilino group), acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkylthio group, arylthio group, sulfamoyl group, alkylsulfonyl group, or carbamoyl group; Z_5 represents oxygen atom, sulfur atom, or $-N(R_{217})-$, where R_{217} represents hydrogen atom, alkyl group, aryl group, or hetero-ring group; "bb" represents an integer of 1 to 4; provided that if "bb" is a plural number, the R_{216} groups in the number "bb" may be the same or different;

R_{218} represents hydrogen atom, halogen atom, alkyl group, aryl group, acylamino group, alkylsulfonylamino group, arylsulfonylamino group, alkoxycarbonyl group, aminocarbonylamino group, carbamoyl group, or sulfamoyl group; R_{220} and R_{223} independently represent hydrogen atom, halogen atom, acylamino group, alkoxycarbonylamino group, aminocarbonylamino group, alkylsulfonylamino group, or arylsulfonylamino group;

R_{219}, R_{221}, and R_{222} independently represents hydrogen atom, chlorine atom, bromine atom, alkyl group, or acylamino group; and

R_{224} represents an alkyl group, aryl group, cyano group or alkoxycarbonyl group

wherein when R_{201} to R_{224} in the formulas DS-1 to DS-9 are groups with a possibility of additional substitution, R_{201} to R_{223} may have additional substituents, the substituents are the same as those listed in the description of the substituent for the hetero-ring group represented by "A" according to claim 1.

4. The hair dyeing composition according to any one of the claims 1 to 3, wherein the azo dye of the formula (I) as defined in claim 1 is present in an amount of 0.0001 to 20 % by weight, based on the whole composition.

5. The hair dyeing composition according to any one the claims 1 to 4, further containing at least one direct dye other than the azo dye of the general formula (I) as defined in claim 1 and/or at least one oxidative dye.

6. The hair dyeing composition as claimed in claim 5, wherein the total amount of the dyes present in said composition is 0.0001 to 20 % by weight, based on the whole composition.

7. The hair dyeing composition according to any one of the claims 1 to 6, further containing an alkaline agent in an amount of 0.01 to 20 % by weight, based on the whole composition.

8. The hair dyeing composition as defined in any one of the claims 5 to 7, being a one part composition, a two part composition or a three part composition, wherein the two part composition comprises a first part containing an alkaline agent and a second part containing an oxidative agent, and wherein the three part composition contains the said first and second parts and additionally a third part containing a powdery oxidizing agent, wherein in each of the said composition the direct dye having the formula (I) may be contained in either one of the respective parts or in each part.

9. Method for dyeing human or animal hair, comprising applying a composition comprising an azo dye represented by the formula (I) to the hair, rinsing the hair after completion of the dyeing and drying the hair:

$$A\text{-}N{=}N\text{-}B \quad (I)$$

wherein A represents a phenyl or naphthyl group, wherein these groups may be substituted, wherein these phenyl or naphthyl groups do not contain sulfo or carboxyl groups or quaternary ammonium groups; and B represents an aromatic group required for the compound represented by the general formula (I) to form a dissociative azo dye which is free from anionic sulfo or carboxyl groups and quaternary ammonium groups.

10. Use of an azo dye represented by the formula (I)

$$A\text{-}N{=}N\text{-}B \quad (I)$$

wherein A represents a phenyl or naphthyl group, wherein these groups may be substituted, wherein these phenyl or naphthyl groups do not contain sulfo or carboxyl groups or quaternary ammonium groups; and B represents an aromatic group required for the compound represented by the general formula (I) to form a dissociative azo dye which is free from anionic sulfo or carboxyl groups and quaternary ammonium groups, for dyeing human or animal hair.

ABSTRACT

The present invention is directed to a hair dyeing composition comprising a dissociative azo dye of the following general formula (I)

A-N=N-B (I)

wherein A represents a phenyl or naphthyl group, wherein these groups may be substituted, wherein these phenyl or naphthyl groups do not contain sulfo or carboxyl groups or quaternary ammonium groups; and B represents an aromatic group required for the compound represented by the general formula (I) to form a dissociative azo dye which is free from anionic sulfo or carboxyl groups and quaternary ammonium groups. Additionally, the present invention describes a method of dyeing human or animal hair by using such a dye and the use of this direct azo dye for dyeing human or animal hair. The use of this direct azo dye can impart the hair with an extremely vivid color and has a less color fade over the time.